HIGH PRESSURE SPIN-LATTICE-RELAXATION TIME STUDIES IN SUPERCOOLED H_2O AND D_2O ENRICHED WITH O-17

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The spin-lattice relaxation times (T_1) have been studied for the $^{17}_{8}O$-nuclei in light and heavy water in the temperature range between 240 K and 450 K and at pressures up to 250 MPa (1). Furthermore ^{1}H spin-lattice relaxation times have been measured in $H_2{}^{17}O$ enriched to 25 % and 50 % with $^{17}_{8}O$ in the temperature range 193 K to 343 K and pressures up to 250 MPa.

The experimental difficulties in studying supercooled water are significantly reduced when it is possible to apply the measurements to water emulsions. NMR-measurements can take full advantage of the emulsion technique. Thereby small waterdroplets are suspended in an insoluble carrier (50 % w/w cyclohexane/cyclopentane) and prevented from coalescing by emulsification with sorbitan tristearate. The sample is contained in a strengthened glass capillary which is incorporated in a Cu/Be-high pressure cell described previously (2). From the O-17 T_1s obtained the orientational correlation times τ_θ, which are the zero-frequency Fourier transforms of the corresponding spectral density functions, have been calculated within the rotational diffusion model. The water molecules have been treated as spherical-tops and are assumed to reorient isotropically on the average. Experimental evidence supporting these assumptions has been presented elsewhere (3). In the course of the calculation of these effective correlation times τ_θ a value of $\frac{e^2qQ}{h}$ = (6,6±0,1) MHz for the O-17 quadrupole coupling constant (QCC) has been used in accordance with the result found for ^{2}H-QCC in supercooled heavy water (4). This assumption has recently been corroborated by Halle and

Wennerström (5). The effective correlation times τ_θ increase with decreasing temperature in a non-Arrhenian fashion. Their pressure dependence reveals a decrease with increasing pressure with a pressure coefficient that increases with falling temperature at low pressures. In the pressure range p = 150-200 MPa they run through a minimum and further increase with raising pressure as is normally found in liquids. Furthermore the effective correlation times τ_θ in $D_2{}^{17}O$ are identical at the respective temperatures and pressures to the effective correlation times τ_θ calculated from ^2H-T_1 measurements in D_2O. This result strongly supports the isotropic nature of the orientational fluctuations of the water molecules. However it does not rule out the possibility of anisotropic rotational motion on a shorter time scale.

Thus at low pressures ($p \leq 150$ MPa) the different isobars can be described with a fractional power law $\tau_\theta = \tau_s\left(\frac{T-T_s}{T_s}\right)^{-\gamma}$ with a singular temperature T_s implying a λ-like anomaly in supercooled water (6). The effective correlation times τ_θ in $H_2{}^{17}O$ are found to be shorter than those in $D_2{}^{17}O$. However at low pressures they could also be fitted to the fractional power law mentioned above, all parameters being equal except the singular temperatures T_s which were found to be lower by about 7 K in light water. This shows that the large dynamic isotope effect found can in the low pressure region be accounted for by the influence of the isotopic substitution upon the singular temperature. The influence of the isotope effect upon the dynamic behaviour of the watermolecules in supercooled water at low pressures is discussed.

At high pressures ($p \geq 200$ MPa) the temperature dependence of τ_θ resembles the dynamics of normal viscous liquids (7). It could be described by the VTF-equation $\tau_\theta = \tau_0 \exp\,(B/T-T_0)$ which implies a divergence of τ_θ at the ideal glass transition temperature T_0. The latter has also been found to be lower in H_2O than in D_2O by about 5 K. In the high pressure region the dynamic isotope effect becomes more complicated in that it does not only appear in the characte-

ristic temperatures T_0 but also in the other parameters. The results are discussed in terms of a constantly rearranging random network of hydrogen-bonded molecules. In addition proton spin-lattice re-

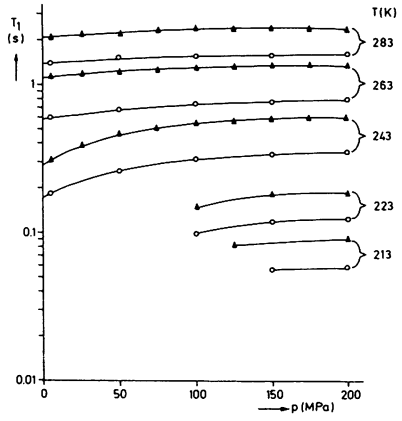

Fig. 1: Isotherms of proton spin-lattice relaxation times in supercooled $H_2{}^{16}O$ (Δ) and $H_2{}^{17}O$ (o) with 50 % O-17 enrichment (Δ) data from ref. (8)

laxation times have been measured in $H_2{}^{17}O$ enriched with 25 % and 50 % O-17 respectively. The data have been analyzed with the assumption that the interaction between O-17 and the protons is to a first approximation an additional intramolecular relaxation path which leads to a shorter relaxation time T_1 than in $H_2{}^{16}O$. Fig. 1 shows a few ^1H-T_1 isotherms in $H_2{}^{16}O$ and $H_2{}^{17}O$ (50 % enriched). Thus the difference between $T_1(H_2{}^{17}O) - T_1^{-1}(H_2{}^{16}O)$ measures a purely intramolecular relaxation rate from which the effective correlation times τ_θ can be extracted. In the temperature range of overlap these effective correlation times τ_θ are identical at the respective temperatures and pressures to the correlation times calculated from the O-17 T_1 in $H_2{}^{17}O$. With these correlation times the intra- and intermolecular contributions to the measured relaxation times T_1 in $H_2{}^{16}O$ can be evaluated. Analysis of the data shows, that in the supercooled liquid the ^1H-relaxation is dominated by the intramolecular contribution. This indicates that translational diffusion is slowed down much more rapidly than is rotational diffusion.

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